(Z)-6-[(2-Fluorophenyliminio)methylene]-2,3-dihydroxyphenolate

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The title compound, $C_{13}H_{10}FNO_3$, crystallizes in a zwitterionic form. The dihedral angle between the aromatic rings is 21.69 (9)°. O—H···O hydrogen bonds generate a centrosymmetric $R_2^2(10)$ dimer and the dimers are linked by O—H···O hydrogen bonds into sheets parallel to (10$\bar{1}$).

Comment

Schiff base compounds are often used as ligands in coordination chemistry because of their metal binding ability and they play an important role in various fields of chemistry and biochemistry (Calligaris & Randaccio, 1987; Lozier et al., 1975; Garnovskii et al., 1993). Some Schiff bases derived from salicylaldehyde have attracted the interest of chemists and physicists because they show thermochromism and photochromism in the solid state (Hadjoudis et al., 1987). Photochromic compounds are of great interest for the control and measurement of radiation intensity, optical computers and display systems (Dürr & Bouas-Laurent, 1990). It has been proposed that molecules showing thermochromism are planar, while those showing photochromism are non-planar (Moustakali-Mavridis et al., 1978). In general, Schiff bases exhibit two possible tautomeric forms, viz. the phenol–imine (or benzenoid) and keto–amine (or quinoid) forms. Another form of the Schiff base compounds is their zwitterionic form, and this form is rarely seen in the solid state (Krygowski et al., 1997).

(I)
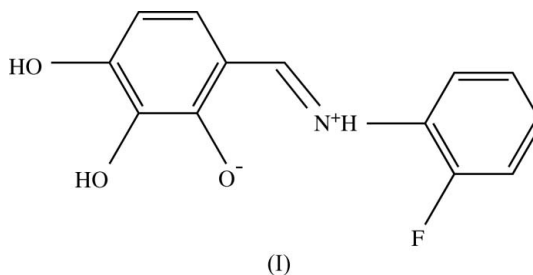
The molecular structure of (I) is shown in Fig. 1. The molecule is in a zwitterionic form with a strong intramolecular N—H···O hydrogen bond (Table 1). Although the N^+—H bond length [1.11 (3) Å] is in agreement with a similar zwitterion (Wojciechowski et al., 2003), the C—O^- bond [1.323 (2) Å] is somewhat shorter than its expected value of 1.3500 (17) Å for a C— single bond (Yüce et al., 2004). This short distance in addition to the shortening of C4—C5 [1.360 (3) Å] and C2—C3 [1.381 (3) Å] and the lengthening of the C1—C2 [1.395 (3) Å], C1—C6 [1.421 (3) Å] and C5—C6 [1.405 (3) Å] bonds is explained by a quinonoid resonance
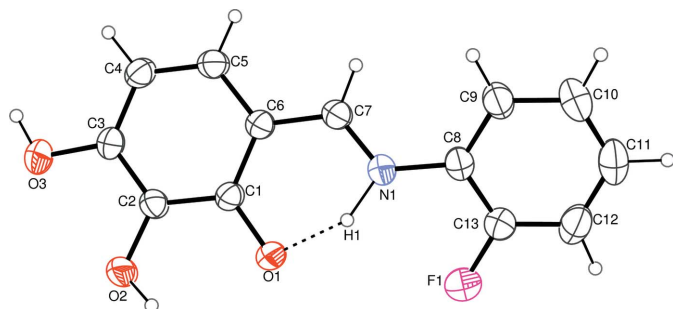
Figure 1
The molecular structure of (I), with the atom-numbering scheme and 30% probability displacement ellipsoids. The dashed line indicates an N—H···O hydrogen bond.
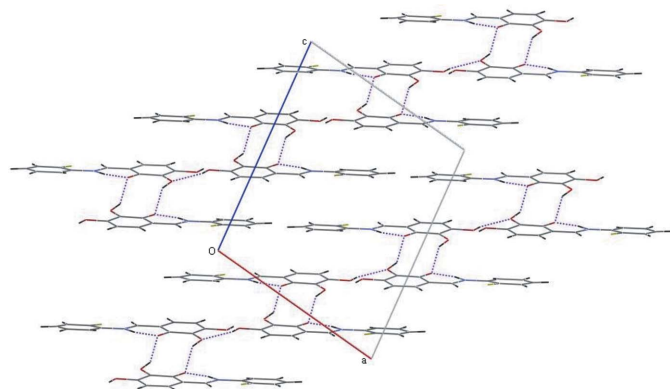

Figure 2
The crystal packing of (I), viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

contribution to the ring containing O^- in the *ortho* position. The N1—C7, N1—C8 and C6—C7 bond distances are as expected [1.295 (2), 1.412 (2) and 1.419 (3) Å, respectively]. In the zwitterionic form, the title compound is non-planar and the dihedral angle between the aromatic rings is 21.69 (9)°.

Molecules of the title compound are linked into centro-symmetric $R_2^2(10)$ dimers by paired O2—H2···O1^{ii} hydrogen bonds (Table 1), and these dimers are linked by O3—H3···O2^{i} hydrogen bonds into sheets parallel to (10$\bar{1}$) (Fig. 2).

Experimental

2,3,4-Trihydroxybenzaldehyde (0.1 g 0.65 mmol) in ethanol (20 ml) was added to a solution containing 2-fluoroaniline (0.072 g 0.65 mmol) in ethanol (20 ml). The reaction mixture was stirred for 1 h under reflux. The resulting precipitate was filtered off and crystals of (I) suitable for X-ray analysis were obtained from chloroform by slow evaporation (yield 82%, m.p. 468–470 K).

Crystal data

$C_{13}H_{10}FNO_3$
$M_r = 247.22$
Monoclinic, $P2_1/n$
$a = 11.5456 (11)$ Å
$b = 6.8521 (4)$ Å
$c = 14.0447 (14)$ Å
$\beta = 101.185 (8)°$
$V = 1089.99 (16)$ Å^3
$Z = 4$
$D_x = 1.506$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 296$ K
Plate, red
$0.77 \times 0.36 \times 0.06$ mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
  $T_{min} = 0.937$, $T_{max} = 0.992$
12517 measured reflections
2076 independent reflections
1263 reflections with $I > 2\sigma(I)$
$R_{int} = 0.125$
$\theta_{max} = 27.2°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.124$
$S = 0.96$
2076 reflections
204 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.030 (6)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	1.11 (3)	1.53 (3)	2.554 (2)	150 (3)
O3—H3···O2^{i}	0.88 (3)	2.01 (3)	2.737 (2)	139 (2)
O2—H2···O1^{ii}	0.90 (3)	1.94 (3)	2.740 (2)	147 (2)

Symmetry codes: (i) $-x + \frac{5}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, -y, -z + 1$.

The crystal used for the intensity data collection was of poor quality and was a non-merohedral twin with two reciprocal lattices differently oriented, giving rise to double diffraction spot sets. We were aware of the twin character of this crystal at the data collection stage but we were unable to find untwinned crystals. The two data sets of the twin parts were integrated separately and then scaled to give the combined data set. However, because the partially overlapped reflections could not be integrated separately, the completeness of the data set decreased to 85%; the value of R_{int} is also rather high. All H atoms were located in a difference map and refined freely. The N—H distance is 1.11 (3) Å, and C—H and O—H distances are in the ranges 0.94 (3)–0.97 (2) Å and 0.88 (3)–0.90 (3) Å, respectively. The U_{iso}(H) value for H1 is 0.143 (12) Å^2, and the U_{iso}(H) values for C– and O-bound H atoms are in the ranges 0.054 (6)–0.110 (10) and 0.096 (9) and 0.101 (9) Å^2, respectively.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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